1 **Characterization of organic aerosols from a Chinese Mega-City during winter:**
2 **predominance of fossil fuel combustion**

4 **Md. Mozammel Haque[1,2,3], Kimitaka Kawamura[2], Dhananjay K. Deshmukh[2], Cao**
5 **Fang[1, 3], Wenhuai Song[1,3], Bao Mengying[1,3] and Yan-Lin Zhang[1,3*]**

7 [1] *Yale-NUIST Center on Atmospheric Environment, Department of Applied*
8 *Meteorology, Nanjing University of Information Science and Technology, Nanjing*
9 *210044, China*
10 [2] *Chubu Institute for Advanced Studies, Chubu University, Kasugai 487-8501, Japan*
11 [3] *Key Laboratory of Meteorological Disaster, Ministry of Education & Collaborative*
12 *Innovation Center on Forecast and Evaluation of Meteorological Disasters, Nanjing*
13 *University of Information Science and Technology, Nanjing 210044, China*

16 *Corresponding author*
17 Yan-Lin Zhang
18 E-mail: dryanlinzhang@outlook.com

28 **Abstract**

29   PM$_{2.5}$ aerosol samples were collected from a Chinese mega-city in Nanjing

30 (32.21°N and 118.73°E) during winter and analyzed for more than 100 compounds of

31 twelve organic compound classes. The most abundant classes of compounds are *n*-

32 alkanes (average, 205 ng m^{-3}), followed by fatty acids (76.3 ng m^{-3}), polycyclic

33 aromatic hydrocarbons (PAHs) (64.3 ng m^{-3}), anhydro-sugars (56.3 ng m^{-3}), fatty

34 alcohols (40.5 ng m^{-3}), and phthalate esters (15.2 ng m^{-3}), whereas hydroxy-/polyacids

35 (8.33 ng m^{-3}), aromatic acids (7.35 ng m^{-3}), hopanes (4.19 ng m^{-3}), primary sugars and

36 sugar alcohols (4.15 ng m^{-3}), lignin and resin products (2.94 ng m^{-3}), and steranes (2.46

37 ng m^{-3}) are less abundant. The carbon preference index of *n*-alkanes (0.83-1.38)

38 indicated that they were significantly originated from the fossil fuels combustion.

39 Diagnostic concentration ratios of organic tracers suggested that PAHs and hopanes are

40 mostly originated from coal burning and traffic emissions, respectively in Nanjing

41 urban area. Positive matrix factorization analysis demonstrated that fossil fuel

42 combustion is the major source (28.7%) in Nanjing winter aerosols. Most of the

43 compounds generally showed higher concentrations in nighttime compared to daytime,

44 due to the accumulation process associated with the inversion layers and enhancement

45 of emissions from heavy trucks at night. We conclude that fossil fuel combustion

46 largely influences the winter organic aerosols in urban Nanjing area. Based on the

47 comparison of present results with previous studies, we found that pollution levels on

48 organic aerosols have been decreased in the urban Nanjing atmosphere for the last

49 decade.

50

51 **Keywords:** PM$_{2.5}$, organic compounds, fossil fuel combustion, positive matrix

52 factorization, Chinese urban aerosols.

53

1 Introduction

54
55   Organic aerosol (OA) is one of the major constituents of airborne particulates,

56   accounting for up to 70% of the fine aerosol mass. They can play a crucial role in the

57   radiative forcing of the Earth and more generally to the environment (Kanakidou et al.,

58   2005). In the last two decades, more attention has been paid to identify organic aerosol

59   optical and cloud formation properties that link OA directly to hydrological cycle and

60   thereby sustainability issues (Dusek et al., 2006; Riipinen et al., 2012). They can affect

61   the climate, air quality, human health, visibility, and ecosystems on the local, regional

62   and global scale (Salma et al., 2017). There are two major sources of atmospheric

63   aerosols that include both primary emissions and secondary aerosol formation. Primary

64   organic aerosols (POA) are directly derived from various sources such as biomass

65   burning, fossil fuels combustion, dust particles, microbial activities, and plant materials,

66   etc., whereas secondary organic aerosols (SOA) are formed by the oxidation process of

67   organic species in the atmosphere.

68   Various types of volatile organic compounds (VOCs) are emitted from natural

69   and anthropogenic sources into the atmosphere. VOCs can be further photo-oxidized by

70   OH, NO_x, O_3 to form SOA in the atmosphere (Haque et al., 2016). Both POA and SOA

71   can contribute to the organic particulate matter (PM) formation in the atmosphere,

72   which can significantly control the physicochemical properties of aerosol particles

73   (Kanakidou et al., 2005). The chemical characterization and the contributions of various

74   sources of aerosol particles are essential to figure out the role and potential impacts of

75   OA in the atmosphere. Moreover, OA poses adverse physiological effects on human

76   health causing asthma, bronchitis, cancer, and heart disease, etc. (Pope et al., 2009;

77   Ramírez et al., 2011).

78   Several studies have reported that OA plays an important role in both the direct

79   and indirect aerosol forcing, affecting the earth's radiation balance and global air

80   quality (Cooke et al., 1999; Lohmann et al., 2000; Jacobson, 2001; Chung and Seinfeld,

81   2002). Based on the model study (Chung et al., 2012), black carbon (BC) is a climate-

82   warming agent whereas organic matter (OM) is a cooling agent. The combined climatic

83   effect of BC and OM can balance the radiative forcing. Model simulation proposed that

84   OA can enhance the cloud droplet concentration and act as an important element of

85   aerosol-cloud-climate feedback system (O'Dowd et al., 2004). Particularly, water-

86   soluble organic carbon (WSOC) influences the hygroscopic properties of atmospheric

87   particles and intensifies their cloud condensation nuclei (CCN) activity (Asa-Awuku et

88   al., 2011). Enhanced CCN number concentrations might be increased the indirect

89   radiative forcing by aerosol, resulting in a more reflective cloud formation (Twomey,

90   1977) and less precipitation (Albrecht, 1989). The OA components uptake water vapor

91   and their interactions with the inorganic salts dissolved in the same aqueous phase can

92   alter the water contents and properties of aerosol particles (Kanakidou et al., 2005).

93   Aerosol particles improved with OM can make the aerosol surfaces more hydrophilic or

94   hydrophobic based on the mixing state and aerosol composition, which further modify

95   the CCN activities of particles.

96   The large emissions of atmospheric particles from China have a major effect on

97   regional and global climate changes (Huebert et al., 2003). Atmospheric pollution in

98   China is a serious problem due to its rapid industrialization and urbanization. Globally,

99   one-fourth of anthropogenic POA are originated in China (Cooke et al., 1999). Many

100   studies have been performed to characterize inorganic aerosols from China because the

101   significant dust emissions are familiar from the deserts area of western China. (Bergin

102   et al., 2001; VanCuren and Cahill, 2002). However, studies on OAs of Chinese mega-

103   cities are still poorly understood (Guo et al., 2003; Bi et al., 2003; Yao et al., 2003).

104   Nanjing is a highly industrialized mega-city located in east China with a population of

105   over 8 million where air pollution is a critical problem. Previous studies of Wang et al.

106   (2002a; 2002b) reported that the aerosol mass of fine particles (< 2.5 µm) in Nanjing

107   atmosphere was about 2-4 times higher than the United States Environmental Protection

108   Agency (USEPA) regulations.

109   To better understand the molecular composition and sources of OAs in Chinese

110   urban area, aerosol sampling campaign was carried on a day and night basis in the

111   mega-city of Nanjing during winter period from 11 December 2014 to 11 January 2015.

112   The objective of this study is to determine more than 100 organic compounds including

113   aliphatic lipids, sugar compounds, polycyclic aromatic hydrocarbons (PAHs), hopanes,

114   lignin and resin products, aromatic acids, polyacids, and steranes in the aerosol particles

115   from Nanjing. Their chemical characteristics, diurnal patterns, and potential sources are

116   discussed in comparison with previous studies conducted a decade ago.

117   **2 Experimental**

118   **2.1 Sample collection**

119   PM$_{2.5}$ sampling was performed from the rooftop of a six-story building at

120   Nanjing University of Information Science and Technology, Nanjing, China using

121   medium volume sampler (Laoshan, Quingdao, China) from 11 December 2014 to 11

122   January 2015 (Figure 1). Daytime and nighttime sampling was conducted from 9:30 to

123   21:00 and 21:30 to 9:00, respectively. Total of 62 samples was collected on prebaked

124   (450°C for 6 h) quartz fiber filters (80 mm) with an air flow rate of 100 L min^{-1}. After

125   sampling, the filter samples were wrapped with aluminum foil, transported to the

126   laboratory and stored at -20°C until the analysis.

127   **2.2 Analysis of polar organics**

128   Several polar organic compounds containing COOH and OH groups were

129   analyzed by gas chromatography-mass spectrometry (GC-MS) using solvent extraction

130   followed by TMS-derivatization technique (Table S1). Filter aliquots (6.28 cm^2) were

131   extracted three times with 5 mL of dichloromethane/methanol mixture (2:1) under ultra-

132   sonication for 10 min. The solvent extracts were filtered through quartz wool packed in

133   a Pasteur pipette to remove all insoluble matrixes, concentrated using a rotary

134   evaporator under vacuum and then totally dried under a gentle nitrogen stream. The

135   dried extracts were derivatized with 50 µL of N,O-bis-(trimethylsilyl)trifluoroacetamide

136   (BSTFA) plus 1% trimethylsilyl chloride and 10 µL of pyridine in a glass vial (1.5 mL)

137   with a Teflon-lined screw cap at 70°C for 3h. The C$_{13}$ n-alkane (diluted in n-hexane)

138   was used as an internal standard (1.43 ng µL^{-1}) prior to injection into a GC-MS for

139   identification. Detailed information on the chemical analysis is interpreted elsewhere

140   (Wang and Kawamura, 2005).

141   The derivatives were analyzed using Hewlett-Packard (HP) model 6890 GC

142   coupled to an HP model 5973 mass-selective detector (MSD). The sample was injected

143   into a splitless mode with the injector temperature at 280°C. The GC oven temperature

144   was set at 50°C for 2 min and then increased from 50 to 120°C at 30°C min^{-1}, and then

145   to 300°C at 6°C min^{-1} with a final isothermal hold at 300°C for 16 min. The GC

146   separation was performed on a DB-5MS fused silica capillary column (30 m long ×

147   0.25 mm inner diameter × 0.5 µm film thickness) with a carrier gas of helium (rate 1.0

148   mL min^{-1}). The mass spectrometer was conducted at 70 eV on an electron impact (EI)

149   mode with a scan range from 50 to 650 Daltons (Da).

150   The organic components were determined by comparison with the retention

151   times and mass spectra of authentic standards as well as literature and National Institute

152   of Standards and Technology (NIST) library data of mass fragmentation patterns

153 (Medeiros and Simoneit, 2007). GC-MS relative response factor (RRF) of each

154 compound was calculated using authentic standards and surrogate compounds. We

155 performed a recovery experiment three times and acquired the average value of more

156 than 80% for target compounds. The field blank filters (n = 5) were analyzed by the

157 procedures as described above. The target species were not noticed in the blank filters.

158 The analytical errors based on replicate analyses (n = 5) were <10%.

159 **2.3 Analysis of nonpolar organics**

160 Non-polar organics, including n-alkanes, PAHs, hopanes, and steranes were

161 analyzed using thermal desorption gas chromatography-mass spectrometry (TD-GC-

162 MS) technique. It should be noted that higher recoveries (>90%) were obtained for

163 nonpolar organics using TD-GC-MS compared to TMS-derivatization/GC-MS (<70%)

164 technique. The filter aliquots (3 mm diameter) were cut into two pieces and then placed

165 into a TD quartz tube (78 mm long × 4 mm inner diameter) and spiked with internal

166 standard mixture (isotope-labeled reference compounds) for quantification. The internal

167 standards consisted of 3 deuterated PAHs, e.g., Nap-d_8, Ace-d_{10}, and Phe-d_{10}.

168 Thermal desorption was performed on an Agilent GC-MS system model

169 7890B/5977A. A capillary column (HP-5MS UI, 5% biphenyl/95% dimethylsiloxane,

170 30 m long × 0.25 mm inner diameter × 0.25 µm film thickness) was used to separate the

171 target compounds. The GC oven temperature programmed from 35°C (3 min) to 120°C

172 at 10°C min^{-1}, ramped from 120°C to 146°C at 4°C min^{-1} and continued to 310°C at

173 8°C min^{-1}, then held at 310°C for 16 min. The sample on the filter punch was inserted

174 into the TD tube with the initial temperature at 35°C before running and increased up to

175 300°C manually at 12°C sec^{-1} after starting the analysis. Column flow rate was 2 mL

176 min^{-1} and split flow was 10 mL min^{-1} for the first 3min, then column and split flow rate

177 changed to 1 mL min^{-1} and 25 mL min^{-1}, respectively. The electron ionization mass

178 spectra (70 eV) were conducted on a scan mode range from 50 to 650 Da. The

179 temperatures of the ion source, quadruples and transfer line were set at 310, 150 and

180 310°C, respectively.

2.4 Carbonaceous components analysis

182 Organic carbon (OC) and elemental carbon (EC) were measured using a Sunset

183 Laboratory carbon analyzer following the IMPROVE (Interagency Monitoring of

184 Protected Visual Environments) thermal-optical evolution protocol and assuming

185 carbonate carbon to be insignificant in the sample (Boreddy et al., 2018). An area of

186 1.54 cm^2 of each quartz filter sample was insert in a quartz boat inside the thermal

187 desorption chamber of the analyzer, and then stepwise heating was performed.

188 A filter cut of 3.14 cm^2 of each sample was extracted with 20 mL organic-free

189 ultrapure water (resistivity >18.2 MΩ cm, Sartorius arium 611 UV) under

190 ultrasonication for 30 min. The water extracts were then passed through a membrane

191 disc filter to throw away the insoluble filter matrixes and analyzed for water-soluble

192 organic carbon (WSOC) using a total organic carbon (TOC) analyzer (Shimadzu, TOC-

193 Vcsh) (Boreddy et al., 2018). The analytical errors in the triplicate analyses were within

194 5% for all carbonaceous components and the concentrations reported here were

195 corrected for the field blanks.

3 Results and Discussion

3.1 Diurnal variations and meteorological conditions

198 No significant difference was observed between day- and night-time for organic

199 compounds in winter aerosols from Nanjing urban area (Figure 2, Tables 1 and S1).

200 Nevertheless, concentrations of organic compounds in nighttime were slightly higher

201 than daytime in most of the cases. It is notable that the planetary boundary layer height

202 (PBLH) is generally lower in nighttime than daytime causing higher concentrations of

203 aerosol particles at night. Interestingly, we found high loadings of organics in daytime

204 sample collected on 15 December when PBLH was high (632 m), whereas lower levels

205 of organics were observed in nighttime of 14 December (PBLH = 82.2 m) (Figures 3

206 and S1b).

207   We observed one episode (E1) during 2 - 5 January while $PM_{2.5}$ and all organic

208 compounds showed similar temporal variations with high loadings (Figure 3).

209 Fascinatingly, NO_2 showed high concentration during E1, whereas relative humidity

210 (RH) and ozone (O_3) levels were not high (Figure S1). Our results suggest that NO_2

211 influences the organic molecular compositions in urban aerosols. It is noteworthy that

212 the major source of NO_2 is of vehicular exhaust origin (Kendrick et al., 2015). Previous

213 studies also reported that NO_x could affect SOA formation (Kanakidou et al., 2005;

214 Zhang et al., 2015; Mochizuki et al., 2015). Moreover, PAHs, hopanes, and steranes

215 showed another episode on 23 and 24 December 2014 probably due to the coal

216 combustion event. It should be noted that higher RH (81-88%) and $PM_{2.5}$ levels (152-

217 226 µg m^{-3}) cause less visibility on 29 December (1.7 km), 10 January (1.8 km), and 11

218 January (1.6 km), which might be due to the haze formation. It is remarkable that the

219 levels of organics were not high during these periods (Figures 3 and S1). These results

220 imply that NO_x chemistry is important than aqueous phase chemistry for OAs in the

221 Nanjing atmosphere.

222 **3.2 Carbonaceous components**

223   The results of OC, EC, and WSOC are mentioned in Table 1. The values of OC

224 and EC were found to be 8.76-40.0 µg m^{-3} (ave. 18.6 µg m^{-3}) and 2.41-30.3 µg m^{-3} (8.25

225 µg m^{-3}) in daytime, and 2.98-40.1 µg m^{-3} (19.1 µg m^{-3}) and 0.87-22.9 µg m^{-3} (8.86 µg

226 m^{-3}) in nighttime, respectively. We found that the day and night variations of OC and

227 EC values are also not significant. The mass ratio of OC to EC (OC/EC) is often used to

228 characterize fossil fuels and biomass burning emissions. Several investigators have used

229 OC/EC ratios to classify the sources of carbonaceous aerosols (Ram et al., 2008;

230 Sandradewi et al., 2008; Saarikoski et al., 2008). The higher OC/EC ratios imply that

231 major source of carbonaceous species is from biomass burning, whereas lower ratios are

232 characteristics of emissions from fossil fuels combustion. Sandradewi et al. (2008) have

233 documented an average OC/EC ratio of 1.1 for vehicular emission and 7.3 for wood

234 burning emission. Saarikoski et al. (2008) pointed out OC/EC ratios of 0.71 for

235 vehicular emission and 6.6 for biomass burning. Watson et al. (2001) proposed the

236 OC/EC ratios of 1.1 for vehicular emission, 2.7 for coal combustion and 9.0 for biomass

237 burning emission. The OC/EC ratios ranged from 1.30 to 3.80 with a mean value of

238 2.40 in this study, which is comparable to the values reported for coal combustion and

239 vehicular emission. These results suggest that fossil fuel combustion such as coal

240 combustion and vehicular emissions were the major source of carbonaceous aerosols in

241 Nanjing urban area.

242   The ratios of OC to EC are also used to differentiate the relative contribution of

243 primary vs. secondary sources; high OC/EC ratios (>2.0) were reported for the aerosols

244 with significant contributions of SOA (Kunwar and Kawamura, 2014; Pani et al., 2017).

245 The OC/EC ratio in this study was on average 2.40, suggesting the significant

246 contribution of SOA in Nanjing aerosols that is consistent with PMF results (see section

247 3.4). The concentration range of WSOC was 5.52-26.6 $\mu g\ m^{-3}$ (11.7 $\mu g\ m^{-3}$) in daytime

248 and 2.51-20.2 $\mu g\ m^{-3}$ (11.8 $\mu g\ m^{-3}$) in nighttime. The WSOC/OC ratios often used to

249 discuss the SOA formation via photochemical aging of atmospheric aerosol particles.

250 The WSOC/OC ratios exceeding 0.4 indicate the aged aerosols with the significant

251 contribution of SOA (Boreddy et al., 2018). The average WSOC/OC ratio of 0.64 in the

252 present study indicates that OAs in Nanjing were relatively aged**.**

3.3 Organic molecular compositions

We detected twelve organic compound classes, including sugars, lignin and resin acids, fatty acids, fatty alcohols, n-alkanes, PAHs, hopanes, steranes, glycerol and polyacids, and phthalate esters, and aromatic acids in the aerosol samples from Nanjing. The total concentrations of organics were on average 424 ng m^{-3} in daytime and 555 ng m^{-3} in nighttime with the predominance of n-alkanes followed by fatty acids, PAHs, anhydro-sugars, fatty alcohols, phthalate esters, glycerol and polyacids, aromatic acids, sugars, hopanes, lignin and resin acids, and steranes (Figure 2). Table S1 shows the values of identified organic compounds. Levoglucosan was the single dominant species followed by C$_{16}$ and C$_{24}$ fatty acids, and C$_{29}$ n-alkane (Table S1).

3.3.1 Aliphatic lipid components

The lipid compounds, e.g., fatty acids, fatty alcohols, and n-alkanes are mainly originated from marine or microbial detritus, terrestrial higher plant waxes, and fossil fuels combustion. Homologues of n-alkanes (C$_{13}$-C$_{39}$) were detected with higher concentrations in nighttime (74.8-535 ng m^{-3}, ave. 228 ng m^{-3}) than daytime (97.6-497 ng m^{-3}, 184 ng m^{-3}) with a maximum at C$_{29}$ (14.0 ng m^{-3} during daytime and 17.9 ng m^{-3} during nighttime) in Nanjing aerosols (Tables 1 and S1, Figure 4a). These concentrations are comparable to those reported from urban cities in Hong Kong (195 ng m^{-3}) and Shanghai (259 ng m^{-3}) (Wang et al., 2006), but much higher than the western North Pacific region (0.11-14.1 ng m^{-3}) (Kawamura et al., 2003). Concentration levels of n-alkanes in this study are not significantly different from previous studies in Nanjing (112-265 ng m^{-3}, 172 ng m^{-3} during daytime; 61.0-503 ng m^{-3}, 278 ng m^{-3} during nighttime) (Table 2) (Wang and Kawamura, 2005). n-Alkanes originated from fossil fuel combustion are dominated by low molecular weight (LMW) homologues

277   ($\leq C_{25}$) (Wang et al., 2009), whereas those derived from plant wax are dominated by

278   high molecular weight (HMW) ones (>C_{25}) (Hays et al., 2005).

279   Biogenic *n*-alkanes showed stronger odd/even carbon number predominance

280   with a carbon preference index (CPI) of >5, whereas anthropogenic *n*-alkanes CPI value

281   is usually close to unity (Simoneit et al., 1991a, 2004c). CPI values obtained in this

282   study ranged from 1.18-1.32 (ave. 1.28) in daytime and 1.10-1.37 (1.24) in nighttime,

283   which is close to unity. This result suggests that the major contributor of *n*-alkanes is

284   the anthropogenic activity such as fossil fuels combustion with less contribution from

285   higher plants in Nanjing aerosols. The present CPI values are similar with those from

286   other Chinese urban areas (ave. 1.16) (Wang et al., 2006) and Tokyo (1.10-2.80, ave.

287   1.50) (Kawamura et al., 1995). On the contrary, higher CPI values were reported for

288   Mt. Tai (4.60) (Fu et al., 2008) and Chichi-jima aerosols (4.50) (Kawamura et al.,

289   2003), where *n*-alkanes were mainly originated from terrestrial higher plant waxes.

290   Plant wax derived *n*-alkanes are estimated as the excess of odd homologues minus

291   adjacent even homologues (Simoneit et al., 1991b, 2004c), which is attributable to

292   vascular plant waxes (Tables 1 and S1). Concentrations ranges of higher plant wax

293   derived *n*-alkanes were 2.12-48.1 ng m^{-3} (ave. 15.5 ng m^{-3}) in daytime and 0.86-58.9 ng

294   m^{-3} (17.6 ng m^{-3}) in nighttime, both of which are much lower than total *n*-alkanes,

295   indicating that *n*-alkanes in Nanjing urban area are derived mainly from fossil fuel

296   combustion.

297   A homologous series of $C_{12:0}$-$C_{32:0}$ saturated fatty acids, including two

298   unsaturated fatty acids ($C_{18:1}$ and $C_{18:2}$), were identified in Nanjing samples. The values

299   of total fatty acids ranged from 14.3 to 254 ng m^{-3} (ave. 66.8 ng m^{-3}) during daytime,

300   whereas they ranged from 8.59 to 252 ng m^{-3} (91.3 ng m^{-3}) during nighttime. It is

301   notable that fatty acids are less abundant compared to *n*-alkanes in Nanjing samples

302   (Figure 2). The molecular distributions of fatty acids are observed by a strong even

303   carbon number predominance with C_{max} at $C_{16:0}$ and $C_{24:0}$ (Table S1 and Figure 4b). CPI

304   values of fatty acids are found to be 5.41 in daytime and 5.52 in nighttime samples. A

305   similar distribution pattern has been proposed in marine and continental aerosols

306   (Mochida et al., 2002; Kawamura et al., 2003; Fu et al., 2008). LMW fatty acids

307   ($<C_{20:0}$) are originated from various sources, e.g., vascular plants, microbial sources,

308   and marine phytoplankton, while HMW fatty acids ($>C_{20:0}$) are derived from terrestrial

309   higher plant waxes (Kawamura et al., 2003; Kolattukudy, 1976; Simoneit, 1978).

310   Biomass burning, motor vehicles, and cooking can also be the important sources of fatty

311   acids in urban areas (Fu et al., 2010). The values of $C_{18:1}$ was observed lower in daytime

312   than nighttime, suggesting an enhanced emission to the atmosphere and oxidation with

313   a higher rate in daytime (Kawamura and Gagosian, 1987).

314   Concentration ranges of C_{12}-C_{34} fatty alcohols were 7.30-165 ng m^{-3} (ave. 36.9

315   ng m^{-3}) during daytime and 4.61-129 ng m^{-3} (43.8 ng m^{-3}) during nighttime (Table S1

316   and Figure 2). Their molecular distributions are characterized by a strong even-to-odd

317   carbon number predominance with C_{max} at C_{28} or C_{30} (Figure 4c). We found that the

318   CPI values of fatty alcohols in Nanjing aerosols (2.56-10.3, ave. 5.22 in daytime and

319   3.06-15.5, 6.32 in nighttime) are lower than those of aerosols from Chennai, India

320   (9.75±2.94) (Fu et al., 2010) and Mt. Tai, China (CPIs 7.95-66.5, ave. 25.6 in daytime

321   and 12.2-53.4, 22.8 in nighttime) (Fu et al., 2008). HMW fatty alcohols ($>C_{20}$) are

322   dominant in the terrestrial higher plant, soils, and loess deposits, whereas LMW fatty

323   alcohols ($<C_{20}$) are dominant in marine biota and soil microbes (Simoneit et al., 1991b).

324   Moreover, a large amount of fatty alcohols together with fatty acids and *n*-alkanes can

325   also be derived from biomass burning (Simoneit, 2002). A positive correlation was

326   observed between fatty alcohols and levoglucosan (r = 0.60, p<0.001), indicating that

327   fatty alcohols are partly originated from biomass burning in Nanjing winter aerosols

328   (Figure S2c). This conclusion is further supported by the factors resolved by PMF

329   analysis, where high loading of fatty alcohols was found with a biomass burning tracer

330   levoglucosan.

331   **3.3.2 Biomass burning tracers**

332   Levoglucosan, galactosan, and mannosan are class of anhydro-sugars, which are

333   produced by the pyrolysis of cellulose and hemi-cellulose (Simoneit, 2002).

334   Levoglucosan is a unique tracer of biomass burning, and has been reported in urban

335   (Wang et al., 2006; Fu et al., 2010; Yttri et al., 2007), marine (Simoneit et al., 2004b;

336   Ding et al., 2013), and polar regions (Stohl et al., 2007; Fu et al., 2009). Levoglucosan

337   is a relatively stable species in the atmospheric aerosol and could be transported long

338   distances (Mochida et al., 2010). We found that levoglucosan is one of the most

339   abundant single tracer among all the identified compounds in the presents tudy, with a

340   concentration range of 4.79-179 ng m^{-3} (ave. 38.4 ng m^{-3}) during daytime and 4.96-354

341   ng m^{-3} (66.0 ng m^{-3}) during nighttime (Tables 1 and S1, Figure 5a), although the values

342   are lower than previous results reported in Nanjing (Wang and Kawamura, 2005).

343   Levoglucosan could account for up to 90% of total sugars in Chinese urban

344   aerosols (Wang et al., 2006). The contribution of levoglucosan to OC and WSOC were

345   0.02-0.51% (ave. 0.09%) and 0.03-0.57% (0.13%) in daytime and 0.02-0.48% (0.13%)

346   and 0.03-0.78% (0.22%) in nighttime, respectively. The amount of galactosan was

347   found to be 0.65-7.47 ng m^{-3} (ave. 2.26 ng m^{-3}) during daytime and 0.48–7.75 ng m^{-3}

348   (3.13 ng m^{-3}) during nighttime, whereas those of mannosan were 0.36-4.30 ng m^{-3} (1.62

349   ng m^{-3}) in daytime and 0.27-5.73 ng m^{-3} (2.06 ng m^{-3}) in nighttime (Table S1 and Figure

350   5a). Galactosan and mannosan were also detected in the aerosol samples. Levoglucosan

351   showed similar temporal trends and strong correlations with galactosan (r = 0.87,

352   p<0.001) and mannosan (r = 0.84, p<0.001) (Figure S2a). It should be noted that the

353   levoglucosan level in this study is 4-6 times lower than that of a previous study in

354   Nanjing (Table 2) (Wang and Kawamura, 2005). This result implies that biomass-

355   burning emissions have been decreased significantly in the last decade in the Nanjing

356   area during winter.

357   We detected four lignin and resin products, i.e., 4-hydroxybenzoic, vanillic

358   syringic, and dehydroabieticacids, which have been used as biomass-burning tracers

359   (Simoneit et al., 2004c). Lignin is a wood polymer, which can produce phenolic acids

360   during burning whereas dehydroabietic acid is more specific to conifer resin (Simoneit,

361   2002). We found that 4-hydroxybenzoic acid was dominant among all lignin and resin

362   products identified in Nanjing samples (Figure 5b). The concentration ranges of 4-

363   hydroxybenzoic, vanillic and syringic acids in day- and night-time were 0.65-4.31 ng m^{-3}

364   (ave. 1.80 ng m^{-3}) and 0.62-4.96 ng m^{-3} (2.01 ng m^{-3}), 0.04-0.92 ng m^{-3} (0.25 ng m^{-3})

365   and 0.08-0.66 ng m^{-3} (0.25 ng m^{-3}), and 0.04-0.57 ng m^{-3} (0.17 ng m^{-3}) and 0.05-0.43 ng

366   m^{-3} (0.20 ng m^{-3}), respectively. The value of dehydroabietic acid was observed 0.11-

367   1.16 ng m^{-3} (0.46 ng m^{-3}) during daytime and 0.00-8.29 ng m^{-3} (0.93 ng m^{-3}) during

368   nighttime. The levels of lignin and resin acids in this study are 1-10 orders of magnitude

369   lower than those from India (Fu et al., 2010) and China (Wang et al., 2006). Lignin

370   products showed strong correlations with levoglucosan (r = 0.60-0.72, p<0.001),

371   suggesting the similar sources and origins. In contrast, there is no correlation of

372   dehydroabietic acid with levoglucosan (r = 0.07), indicating a different source of

373   dehydroabietic acid in Nanjing aerosols. The low concentrations of dehydroabietic acid

374   imply that boreal conifer forest fires are not important for the Nanjing aerosols.

375   **3.3.3 Primary sugars and sugar alcohols**

376   Sugar compounds are considered as tracers for primary biological aerosol

377 particles, which are water-soluble and thus contribute to WSOC in aerosol particles

378 (Elbert et al., 2007; Medeiros et al., 2006; Yttriet al., 2007). Four primary sugars

379 (glucose, fructose, trehalose, and sucrose) and four sugar alcohols (erythritol, arabitol,

380 mannitol, and inositol) were identified in the aerosol samples from Nanjing. The sugar

381 compounds are generated from micro-organism (pollen, fungi, and bacteria), plants,

382 flowers, resuspension of surface soil and unpaved road dust (Graham et al., 2003;

383 Simoneit et al., 2004a; Yttri et al., 2007). They can also be originated during biomass

384 burning. Total concentrations of primary sugars measured were 0.78-7.02 ng m^{-3} (ave.

385 2.90 ng m^{-3}) in daytime and 0.50-6.58 ng m^{-3} (2.98 ng m^{-3}) in nighttime, whereas those

386 of sugar alcohols were 0.30-2.90 ng m^{-3} (1.16 ng m^{-3}) during daytime and 0.19-2.75 ng

387 m^{-3} (1.27 ng m^{-3}) during nighttime.

388   Most primary sugars exhibited higher concentrations in daytime than nighttime

389 except for glucose (Figure 5c). Graham et al. (2003) proposed that fructose and glucose

390 along with sucrose are emitted as fern spores, pollen, and other "giant" bioaerosol

391 particles in daytime. Glucose showed a significant correlation with levoglucosan (r =

392 0.75, p<0.001) (Figure S2d), indicating that it is associated with biomass burning,

393 which can interpret high levels of glucose in nighttime, whereas other primary sugars

394 showed weak correlations with levoglucosan (r = 0.05-0.09). Biomass burning as a

395 source of glucose has also been proposed by Fu et al. (2008). Trehalose is mostly

396 derived from microorganisms such as bacteria, fungi, and yeast and also small amount

397 from higher plants, and invertebrates (Medeiros et al., 2006). It is also considered as a

398 product of unpaved road dust and resuspension of surface soil (Simoneit et al., 2004b;

399 Wang and Kawamura, 2005).

400   On the contrary, all sugar alcohols presented higher concentrations in nighttime

401   than in daytime while the scenario is opposite for primary sugars. Significant

402   correlations were observed between sugar alcohols and levoglucosan (r = 0.51-0.75,

403   p<0.001), suggesting a contribution of biomass burning to primary bio-aerosol particles,

404   which can explain their higher concentrations in nighttime. Previous articles proposed

405   that a huge amount of sugars and sugar alcohols can be emitted through the combustion

406   of green vegetation from temperate forests (Medeiros and Simoneit, 2008). The sugar

407   polyols are produced mainly from microbial sources, e.g., fungi, bacteria. They can also

408   release from the bark of trees, leaves, and branches. The values of sugar compounds in

409   this study are lower than other Chinese urban areas (Wang et al., 2006).

410   **3.3.4 Polycyclic aromatic hydrocarbons**

411   PAHs have severe health effect due to their genotoxicity and carcinogenicity.

412   These aromatic compounds are mainly emitted from anthropogenic activities, including

413   biomass burning, coal combustion, vehicular emissions, and natural gas combustion.

414   PAHs showed a weak positive correlation with levoglucosan (r = 0.20), suggesting that

415   there is no serious contribution of PAHs from biomass burning activities in Nanjing

416   aerosols. Total seventeen PAHs were identified in the Nanjing samples with the

417   concentration range of 29.5-106 ng m^{-3} (ave. 54.5 ng m^{-3}) in daytime and 21.7-223 ng

418   m^{-3} (72.5 ng m^{-3}) in nighttime (Tables 1 and S1, Figure 2). The higher concentrations of

419   PAHs in nighttime might be due to the lower dispersion of the boundary layer at night

420   (Figure 6a).

421   Furthermore, heavy-duty trucks that are permitted by the local government to

422   work only at night as well as coal combustion should contribute to higher

423   concentrations of PAHs into the air in nighttime. Our values are 3-4 times higher than

424   those found in Hong Kong (14 ng m^{-3}) but lower than those in Beijing winter aerosols

425 (208 ng m^{-3}) (Wang et al., 2006). Fluoranthene was found as a dominant PAH (ave.

426 8.24 ng m^{-3}) in Nanjing aerosol samples followed by chrysene (6.72 ng m^{-3}), pyrene

427 (6.42 ng m^{-3}) and benzo(b)fluoranthene (BbF) (5.85 ng m^{-3}) (Figure 6a). Wang et al.

428 (2007a) proposed that coal burning was the dominant source for PAHs in Chinese urban

429 aerosols. However, traffic emissions are also an important source for PAHs in Chinese

430 urban areas (e.g., Guangzhou, 2003) during winter (Wang et al., 2006).

431 PAHs can be further photooxidized to form SOA, i.e., phthalic acid in the

432 atmosphere (Zhang et al., 2016). Ding et al. (2007) proposed that PAHs could be

433 degraded during long-range transport. Therefore, the ratios of PAH isomer pairs can be

434 used to interpret the chemical aging of PAHs in the atmosphere. Benzo[a]anthracene

435 (BaA) and benzo(a)pyrene (BaP) are expected to be degraded more easily than their

436 isomers during transportation due to their higher reactivity. Thus, the lower ratios (<1.0)

437 of benzo[a]anthracene (BaA)/chrysene (Chry) and benzo(a)pyrene (BaP)/

438 benzo(e)pyrene (BeP) indicate relatively more photochemical processing of PAHs. The

439 ratios of BaA/Chry and BaP/BeP were calculated 0.79 and 0.88, respectively, which

440 imply that PAHs of Nanjing aerosols were more aged due to the atmospheric

441 transportation from long distances.

442 Characteristic ratios of PAHs are indicative of their specific sources. Previous

443 studies (Wang et al., 2007a, 2009; Bi et al., 2005) pointed out that the concentration

444 ratios of indeno(1,2,3-cd)pyrene to benzo(ghi)perylene (IP/BghiP), and

445 benzo(ghi)perylene to benz(e)pyrene (BghiP/BeP), are indicative of different emission

446 sources (Table 3). The ratios of IP/BghiP nearby 0.22, 0.50 and 1.3 are attributable to

447 gasoline, diesel, and coal combustion sources, respectively. On the other hand,

448 BghiP/BeP ratio of 2.0 indicates mobile exhausts and 0.8 indicates coal combustion

449 emissions (Grimmer et al., 1983; Ohura et al., 2004). Furthermore, the

450 fluoranthene/(fluoranthene+pyrene) (Flut/(Flut + Pyr)) ratios of 0.46-0.56 indicate

451 vehicular emissions, especially from catalytic converter-equipped automobiles (0.44),

452 whereas IP/(BghiP+IP) ratios (0.18, 0.37 and 0.56) are for cars, diesel, and coal

453 combustion, respectively (Bi et al., 2005).

454   In this study, we found the ratios of IP/BghiP, Bghi/Bep, Flut/(Flut + Pyr), and

455 IP/(IP+BghiP) are 1.23, 1.17, 0.56, and 0.55, respectively. The ratios are closer to those

456 in coal burning emissions than in vehicular exhausts. These results imply that PAH

457 components in Nanjing winter aerosols are mainly derived from coal combustion. The

458 PAH compositions of our study are different from those reported from Sacramento

459 (Kleeman et al., 2008), Los Angeles and London (Finlayson-Pitts and Pitts Jr, 2000), in

460 which BghiP/BeP ratios are 5.6, 3.5 and 1.7, respectively, when vehicular emissions

461 were the major sources for PAHs in these cities. The present PAH concentrations in

462 Nanjing aerosols are lower than those found in a previous study from Nanjing samples

463 collected in 2004 (Table 2) (Wang et al., 2007a) and one-fourth of those collected in

464 2001 (214 ng m^{-3}) (Yang et al., 2005), indicating the local air quality in Nanjing is

465 improving since 2001.

466 **3.3.5 Hopanes and Steranes**

467   Hopane and sterane isomers are considered as biomarkers of fossil fuel

468 emissions, which belong to the higher boiling fraction of crude oil and are more

469 resistant to degradation than *n*-alkanes. They are abundantly originated from the crude

470 oil and engine oil, and consequently in vehicle exhaust from unburned lubricating oil

471 residues and road dust (Ding et al., 2009). Six hopane compounds were identified in the

472 Nanjing urban samples (Table S1) with higher levels in nighttime (0.13-26.1 ng m^{-3},

473 ave. 4.16 ng m^{-3}) and lower levels in daytime (0.09-20.8 ng m^{-3}, 3.78 ng m^{-3}) (Figure 2).

474 The concentrations of hopane in the present study are comparable with those from other

475   Chinese cities and Tokyo (0.7-15 ng m^{-3}; 5.5 ng m^{-3}) (Wang et al., 2006). Wang et al.

476   (2009) reported that concentrations of hopanes in the urban samples were 2 orders of

477   magnitude higher than those in the mountain samples whereas hopanes were not

478   detectable in the marine samples.

479   The diagnostic ratios of hopanes can differentiate their sources (Table 3). The

480   17α(H)-21β(H)-29-norhopane (C$_{29}\alpha\beta$)/17α(H)-21β(H)-hopane (C$_{30}\alpha\beta$) ratios of 0.59-

481   0.66, 0.42, and 0.58-2.0 are attributable to gasoline, diesel and coal burning emissions,

482   respectively (Rogge et al., 1993a; Oros and Simoneit, 2000). In addition, the ratios of

483   17α(H)-21β(H)-22S-homohopane/(17α(H)-21β(H)-22S-homohopane + 17α(H)-21β(H)-

484   22R-homohopane) [C$_{31}\alpha\beta$S/(C$_{31}\alpha\beta$S + C$_{31}\alpha\beta$R)] ranging from 0.60-0.62, 0.50, and

485   0.05-0.37 indicate gasoline, diesel and coal burning emissions, respectively (Rogge et

486   al., 1993a; Oros and Simoneit, 2000). We observed that concentration ratios of

487   C$_{29}\alpha\beta$/C$_{30}\alpha\beta$ and C$_{31}\alpha\beta$S/(C$_{31}\alpha\beta$S+ C$_{31}\alpha\beta$R) in this study are 0.58 and 0.48,

488   respectively, which are near to those in vehicular emissions than coal combustion. Thus,

489   hopanes in the Nanjing aerosol are predominantly emitted from traffic emissions due to

490   rapidly increasing of automobiles in Chinese mega-cities.

491   A series of steranes were also identified in the present study. Concentration

492   ranges of total steranes were 1.14-9.16 ng m^{-3} (ave. 2.29 ng m^{-3}) during daytime and

493   1.09-11.1 ng m^{-3} (2.64 ng m^{-3}) during nighttime. The diurnal distribution patterns of

494   steranes showed remarkable similarity with hopanes. The strong correlation coefficient

495   was also observed between steranes and hopanes (r = 0.94, p<0.001), indicating their

496   similar emission sources (Figure S3d). It is reasonable because homologues of hopanes

497   and steranes are very stable and have similar atmospheric fates (Ding et al., 2009). In

498   contrast, PAHs showed positive correlations with hopanes and steranes with a lower

499   correlation coefficient (r = 0.42, p<0.001), indicating their partly similar sources.

3.3.6 Phthalates

Phthalates are common additives widely used as a softener and plasticizers in polyvinylchloride (PVC) and synthetic polymers, respectively. It can be emitted into the atmosphere through the evaporation process due to their weak bonding in the polymer. Phthalates have potential health effect due to their endocrine disrupting and carcinogenic properties (Sidhu et al., 2005). It is necessary to pay attention to phthalates as toxic components in the aerosol particles. However, few studies have reported their atmospheric distribution over China (Fu et al., 2008; Wang et al., 2006, 2007a). Four phthalate esters, i.e., diethyl (DEP), di-iso-butyl (DiBP), di-n-butyl (DnBP), and di-(2-ethylhexyl) (DEHP) phthalates were characterized in this study with total concentrations of 13.9 ng m^{-3} (range, 2.66-40.0 ng m^{-3}) in daytime and 16.3 ng m^{-3} (3.79-51.8 ng m^{-3}) in nighttime (Figure 7a). DnBP (ave. 8.07 ng m^{-3}) is the dominant tracer, followed by DEHP (4.00 ng m^{-3}), DiBP (2.59 ng m^{-3}) and DEP (0.14 ng m^{-3}). The levels of phthalates in this study are 4-20 times lower than those proposed in other Chinese megacities in 2006 (Wang et al., 2006), although comparable than those observed from Paris, France (8.2 ng m^{-3}) (Teil et al., 2006), Sweden (3.7 ng m^{-3}) (Thuren and Larsson, 1990), and Texas, USA (2.1 ng m^{-3}) (Weschler, 1984).

The evaporation of phthalates can be accelerated under high ambient temperature conditions. The higher values in nighttime than daytime of phthalates in Nanjing aerosol is opposite with the result of Mt. Tai aerosols (Fu et al., 2008) due to the decreased PBLH in nighttime. Moreover, there is no significant difference in temperature between day and night during the campaign in Nanjing (Figure S1). Significant correlations were found between DEP and DiBP (r = 0.85, p<0.001) as well as DiBP and DnBP (r = 0.87, p<0.001) (Figures S4a and S4b), suggesting that these compounds are commonly used as plasticizers in China and released in the same way

525   into the atmosphere. It should be noted that the concentration level of phthalates in this

526   study is 1-2 orders of magnitude lower than those found in Nanjing aerosols collected in

527   2004 (ave. 230 ng m^{-3}) (Wang et al., 2007a), suggesting a significant improvement of

528   local air quality in Nanjing regarding plastic emission.

529   **3.3.7 Aromatic acids**

530   We detected benzoic acid and three phthalic acids in the urban aerosols from

531   Nanjing with total concentrations of 6.70 ng m^{-3} (1.53-23.1 ng m^{-3}) in daytime and 8.37

532   ng m^{-3} (1.99-18.5 ng m^{-3}) in nighttime (Figure 7b). These acids can play a significant

533   role to increase the formation of new particles in the atmosphere (Zhang et al., 2004).

534   Benzoic acid ranged from 0.17-0.95 ng m^{-3} (ave. 0.45 ng m^{-3}) in daytime and 0.24-1.22

535   ng m^{-3} (0.54 ng m^{-3}) in nighttime (Table S1), which is 1 and 4 orders of magnitude

536   lower than summertime aerosol of Mt. Tai and wintertime aerosol of tropical India,

537   respectively (Fu et al., 2008, 2010). Benzoic acid is primarily emitted from automobiles

538   (Rogge et al., 1993b; Kawamura et al., 2000) but also been proposed as a secondary

539   component via a photooxidation of several aromatic hydrocarbons (Fu et al., 2010).

540   Total phthalic acids varied from 1.40-21.9 ng m^{-3} (ave. 6.25 ng m^{-3}) during

541   daytime and 1.76-16.8 ng m^{-3} (7.83 ng m^{-3}) during nighttime. Their concentrations are

542   lower than those found during aircraft measurement over China in summer (17±13 ng

543   m^{-3}) (Wang et al., 2007b) but higher than the samples measured from the northwestern

544   Pacific (ave. 1.5 ng m^{-3}) (Simoneit et al., 2004a). The molecular distributions of

545   phthalic acids showed the dominance of terephthalic acid (Figure 7b), which accounted

546   for 82% of total aromatic acids in Nanjing samples. Phthalic acids are SOA products

547   produced from several PAHs (Oliveira et al., 2007; Fine etal., 2004). It is noteworthy

548   that PAHs mostly produce phthalic acids over the North China Plain (Fu et al., 2008).

549   Terephthalic acid can be derived from plastics burning as well (Fu et al., 2010).

550   Aromatic acids showed positive correlations with 4 and 5 rings PAHs (r = 0.56,

551   p<0.001) and phthalates (r = 0.71, p<0.001) (Figure S3c), suggesting that they are

552   primarily derived from PAHs. Furthermore, aromatic acids showed significant

553   correlation with oxidation products of polyacids (r = 0.83, p<0.001) (Figure S4c),

554   indicating the secondary oxidation process is a major source of aromatic acids.

555   However, higher concentrations of aromatic acids in nighttime rather than daytime may

556   not explain photochemical oxidation. We propose two explanations for the high level of

557   SOA products in nighttime. First, SOA products are formed during long-range

558   atmospheric transport that is consistent with aged PAHs in the aerosols as discussed

559   above (section 3.3.4). Second, NOx can play an important role to oxidize PAHs in

560   nighttime when NOx concentration is high (Offenberg et al., 2007; Henze et al., 2008).

561   However, further studies are needed for the justification of NOx influence in the

562   Nanjing atmosphere.

563   **3.3.8 Hydroxy-/polyacids**

564   Glycerol and several polyacids were identified in all the samples from Nanjing

565   (Table S1). Glycerol is a primary product of a metabolic reaction of soil organisms,

566   while polyacids are secondarily produced by photo-oxidation of organic precursors

567   (Simoneit et al., 2004c). Glycerol didn't show significant correlation with polyacids (r =

568   0.21-0.38), implying their different sources (i.e., primary and secondary). Kawamura

569   and Ikushima(1993), and Matsunaga et al. (1999) reported that malic acid is a

570   photooxidation product of succinic acid, which is one of the photooxidation products of

571   biogenic unsaturated fatty acids (BUFAs) in the atmosphere. Moreover, SOA tracers,

572   including malic and tartaric acids are produced by the photochemical oxidation of

573   isoprene (Claeys et al., 2004).

574   The concentration range of glycerol was 0.66-5.99 ng m^{-3} (ave. 2.67 ng m^{-3})

575   during daytime and 0.73-8.72 ng m^{-3} (3.50 ng m^{-3}) during nighttime. Glycerol is a

576   dominant component in this group (Table S1 and Figure7c), which is consistent with

577   the previous report from Nanjing aerosol in 2004-2005, whereas present concentration

578   level is lower than that reported in Nanjing (Wang and Kawamura, 2005).

579   Concentrations ranges of total polyacids were 1.21-23.5 ng m^{-3} (5.1 ng m^{-3}) during

580   daytime and 2.05-11.2 ng m^{-3} (5.80 ng m^{-3}) during nighttime, among which tartaric acid

581   (2.18 ng m^{-3}) was dominant (Figure 7c). Tartaric acid presented a positive correlation

582   with levoglucosan (r = 0.75, p<0.001) (Figure S2b), suggesting an influence of biomass

583   burning. Significant correlations were found among all polyacids (r = 0.50-0.75,

584   p<0.001), indicating their similar source or formation pathway. Polyacids showed a

585   strong correlation with WSOC (r = 0.85, p<0.001) (Figure S4d), indicating their water-

586   soluble and hygroscopic nature and therefore it might influence the CCN activities of

587   aerosol particles. It should be noted that secondary oxidation products are formed

588   during long-range atmospheric transport, which can explain high values of polyacids in

589   nighttime. This result is consistent with the high WSOC/OC ratio in Nanjing aerosols

590   (see section 3.2).

591   **3.4 Source apportionment of organic aerosols using PMF**

592   Positive matrix factorization (PMF5.0, USEPA) analysis was performed in this

593   study for better understanding the sources of the identified components. It is a statistical

594   source apportionment model widely used to verify underlying covariance among

595   chemical parameters (Paatero and Tapper, 1994; Jaeckels et al., 2007). Detailed

596   information of the PMF model can be found elsewhere (Paatero, 1997; Paatero and

597   Tapper, 1994). PMF model was applied for apportioning ambient PM to motor vehicle

598   and wood combustion emission, SOA, and two point sources using organic molecular

599 markers (Jaeckels et al., 2007). This model has also been extensively used for

600 identifying source profile and source contribution of PM based elemental and organic

601 markers data (Song et al., 2001; Buzcu et al., 2003; Jaeckels et al., 2007; Jia et al.,

602 2010). The analytical errors estimated for the measured values of chemical species in

603 PMF analysis are 10%. The detected organic compound classes were subjected to

604 source apportionment evaluation to make the classifications of sources using the model.

605 PMF model application resolved 5 source factors based on Q values that contributed to

606 ambient $PM_{2.5}$ in this study. OC, EC and some inorganic ions were also used to

607 investigate possible different sources. We used $PM_{2.5}$ as the sum of total variables

608 during the model convergence. Figure 8 shows composition source profiles for the five

609 factors resolved by PMF analysis, where factor 3 is a dominant source.

610 Factor 1 is dominated by levoglucosan (69%) followed by fatty alcohol (C_{30})

611 (56%), arabitol (44%) and n-alkane (C_{29}) (34%). Factor 1 is associated with biomass

612 burning because levoglucosan is a specific tracer of biomass burning. Moreover, fatty

613 alcohols, fatty acids, n-alkanes, and sugar compounds can also be emitted from biomass

614 burning. Biomass materials, including rice and wheat straws, and cotton stems, are

615 widely used for domestic cooking in rural areas around Nanjing, particularly in the

616 evening. Therefore, particles from biomass burning are abundantly released into the

617 atmosphere and then transported to the Nanjing urban area. This idea is consistent with

618 high loadings of biomass burning tracers during nighttime.

619 Factor 2 is enriched with nss-Ca^{2+} (75 %), suggesting that the component is

620 associated with soil dust because it is a specific tracer of soil dust (Athanasopoulou et

621 al., 2010; Brahney et al., 2013). Many infrastructures of the urban area are constructing

622 in China, which can produce dust particles largely and emit into the atmosphere. Factor

623 3 is attributed to secondary oxidation products because of the dominant species in this

624   source profile is malic acid (69%). Malic acid is a secondary oxidation product as

625   described above (see section 3.3.8).

626   Factor 4 was abundantly loaded by fluoranthene (representative PAH) (79%),

627    $C_{30}\alpha\beta$ (representative hopane) (64%) and C_{29} (representative *n*-alkane) (50%), implying

628   their origination from the fossil fuel combustion. It should be noted that *n*-alkanes also

629   showed a loading in factor 1, suggesting that *n*-alkanes are partly associated with

630   biomass burning. PAHs can be emitted from fossil fuel combustion and biomass

631   burning activities. However, we observed that PAHs are mainly derived from fossil fuel

632   combustion in Nanjing (see section 3.3.4). Furthermore, *n*-alkanes can be originated

633   from fossil fuel combustion and higher plant waxes, whereas fossil fuel was the

634   dominant source for *n*-alkanes in Nanjing aerosols (see section 3.3.1). Hopanes are

635   emitted from the vehicular exhaust as well as coal burning. Low-quality coals are

636   extensively used in urban and rural areas in China for cooking and house heating. Many

637   power plants in Chinese cities also used a large amount of coal for producing energy.

638   Running vehicles have also increased severely in China, which can emit hopanes in the

639   atmosphere. Factor 5 is dominated by di-(2-ethylhexyl) (DEHP) phthalate (63%)

640   followed by terephthalic acid (35%), which should be associated with plastic burning.

641   Terephthalic acid is a secondary oxidation product and also can be emitted from the

642   open burning of plastics as discussed above.

643   PMF results can be further utilized to calculate the relative contributions of sources

644   to the amount of ambient OC using a multiple linear regression between the isolated

645   factor strengths and measured OC (Song et al., 2001). Results of this analysis are

646   presented in Figure 9. Fossil fuel combustion was the dominant source (28.7%)

647   considering the primary source, followed by emissions of biomass burning (17.1%), soil

648   dust (14.5%), and plastic burning (6.83%) during this study period. However, secondary

649   oxidation products showed the highest contribution (32.9%) to PM$_{2.5}$ in Nanjing

650   probably due to long-range atmospheric transport. These results indicate that fossil fuel

651   combustion is an important contributor to Nanjing aerosol during winter.

652   **4. Summary and Conclusions**

653   We collected PM$_{2.5}$ aerosol samples during winter from Nanjing, an urban area

654   located in east China in 2014 to 2015. Twelve organic compound classes were

655   identified in the aerosol samples with *n*-alkanes as the dominant compound class,

656   followed by fatty acids, PAHs, anhydro-sugars, fatty alcohols, and phthalate esters. The

657   concentrations of organic compounds were slightly higher at night samples than day

658   samples because of the lower PBLH and more emissions from heavy-duty trucks as

659   well as coal and biomass burning in nighttime.

660   The molecular signature of *n*-alkanes with a weak odd-carbon number

661   predominance and maxima of C$_{29}$ (ave. CPI: 1.18) implies their significant emission

662   from fossil fuels combustion. On the contrary, microbial and plant waxes are the major

663   source of fatty acids and fatty alcohols in this study. Fatty alcohols are also significantly

664   emitted from biomass burning. The biomass burning tracer, levoglucosan was the

665   dominant species among the detected compounds. Levoglucosan and other biomass

666   burning tracers are mainly originated from house cooking and heating during study

667   period. Concentrations of secondary oxidation products, including aromatic acids and

668   polyacids, maximized during nighttime possibly because of the influence of NO$_x$ or

669   long-range atmospheric transport.

670   The diagnostic ratios of the tracer compounds suggest that coal burning is the

671   major source of PAHs while hopanes are abundantly emitted from traffic emissions

672   over Nanjing atmosphere. PMF analysis demonstrated that fossil fuel combustion is an

673   important source (28.7%) in Nanjing winter aerosols. The concentrations of organic

674 tracers in this study are lower than previously reported Nanjing aerosols collected in

675 2004-2005. Air quality in Nanjing may have been improved for last decade. However,

676 fossil fuel combustion emissions have not been decreased significantly and still control

677 the compositions of wintertime OAs in Nanjing atmosphere.

678

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1030 **Table 1.** Mean concentrations of identified organic compound classes (ng m^{-3}) and
1031 carbonaceous components (μg m^{-3}) in the atmospheric aerosol samples (PM$_{2.5}$) from Nanjing,
1032 China.
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Compounds	Daytime				Nighttime			
	Mean	Min[a]	Max[b]	SD[c]	Mean	Min[a]	Max[b]	SD[c]
n-Alkanes	177	96.1	467	76.6	218	74.4	500	89.3
Plant Wax Alkanes	15.5	1.12	56.2	11.2	17.6	0	62.1	14.2
Fatty acids	66.8	14.3	254	47.9	91.3	8.57	252	59.2
Fatty alcohols	36.9	7.30	165	29.9	43.8	4.61	129	26.7
Anhydro-sugars	42.3	5.8	191	40.9	71.2	5.71	367	80.1
Sugars	3.44	0.78	8.89	1.75	3.43	0.59	8.49	1.81
Phthalate esters	13.9	2.66	40.0	10.1	16.3	3.80	51.8	11.1
Glycerol and polyacids	7.78	1.59	29.7	6.17	9.30	2.54	23.1	5.79
Aromatic acids	6.70	1.53	23.1	4.69	8.37	1.99	18.4	4.83
Lignin and resin products	2.68	0.84	6.96	1.29	3.39	0.75	14.3	2.70
PAHs	54.5	29.5	106	17.8	74.8	21.7	223	43.8
Hopanes	3.79	0.07	20.8	4.15	4.64	0.13	26.1	5.31
Steranes	2.29	1.13	9.15	1.56	2.65	1.08	11.1	1.92
Total organics	**434**	**163**	**1378**	**254**	**565**	**126**	**1686**	**347**
OC	18.6	8.76	40.0	8.44	19.1	2.98	40.1	8.53
EC	8.25	2.41	30.3	5.46	8.86	8.86	8.86	8.86
WSOC	11.7	5.52	26.6	4.68	18.1	1.51	34.4	8.92
OC/EC	2.47	1.30	3.69	0.54	2.36	1.51	3.76	0.56
WSOC/OC	0.58	0.42	0.78	0.10	0.55	0.40	0.70	0.08

1034 [a]Minimum, [b]Maximum, [c]Standard deviation
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Table 2. Comparisons of the average concentrations (ng m^{-3}) of organic tracers with those measured during 2004-2005 (Wang and Kawamura, 2005; Wang et al., 2007a[b]) in Nanjing aerosols during winter.

Compounds	This study		2004-2005	
	Daytime	Nighttime	Daytime	Nighttime
n-Alkanes	177	218	172	278
Plant Wax Alkanes	15.5	17.6	18.8	20.6
Fatty acids	66.8	91.3	245	338
Fatty alcohols	36.9	43.8	74.5	120
Levoglucosan	42.3	71.2	238	297
Sugars	3.44	3.43	59	53
Phthalate esters[b]	13.9	16.3	158	181
Glycerol and polyacids	7.78	9.30	41.4	41.8
Aromatic acids	6.70	8.37		Not detected
Lignin and resin products	2.68	3.39	24.6	59.0
PAHs[b]	54.5	74.8	69	104
Hopanes[b]	3.79	4.64	7.3	9.9
Steranes	2.29	2.65		Not detected
Total organics	**434**	**565**	**1108**	**1502**

Table 3. Diagnostic concentration ratios of biomarkers for source identification from fossil fuel combustions including gasoline- and diesel cars.

	Present study		Gasoline		Diesel	Coal
	Daytime	Nighttime	Noncatalyst	Catalyst		
IP/BghiP	1.26	1.19	0.22[a]		0.50[a]	1.3[a]
BghiP/Bep	1.21	1.13	2.0[b]			0.8[b]
Flut/(Flut + IP)	0.57	0.56	0.46-0.56[c]	0.44[c]		
IP/(IP + BghiP)	0.56	0.54	0.18[c]		0.37[c]	0.56[c]
$C_{29}\alpha\beta/C_{30}\alpha\beta$	0.65	0.51	0.59[d]	0.66[d]	0.42[d]	0.58-2.0[e]
$C_{31}\alpha\beta S/(C_{31}\alpha\beta S + C_{31}\alpha\beta R)$	0.39	0.57	0.60[d]	0.62[d]	0.50[d]	0.05-0.37[e]

[a]Grimmer et al., 1983, [b]Ohura et al., 2004, [c]Bi et al., 2005, [d]Rogge et al., 1993a, [e]Oros and Simoneit, 2000

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1080   **Figure 1.** A map of sampling site located in Nanjing, China.
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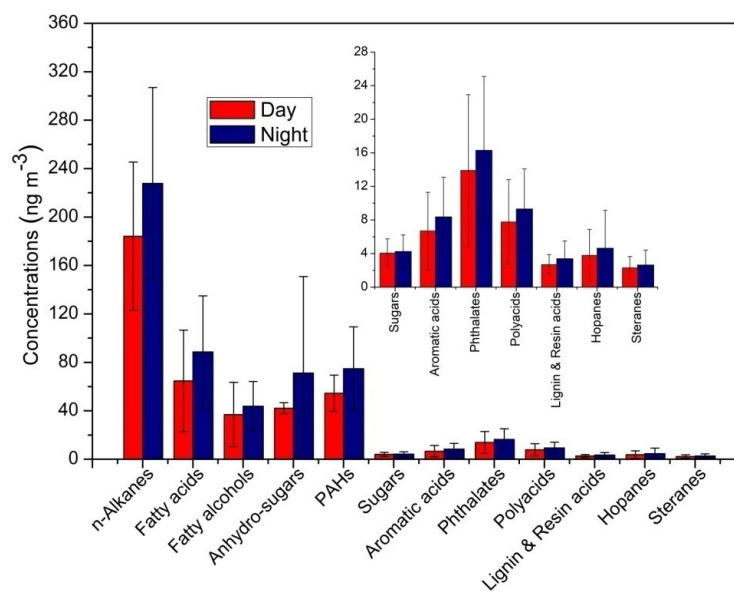
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1085   **Figure 2.** Concentrations of organic compound classes detected in the Nanjing
1086   aerosols.
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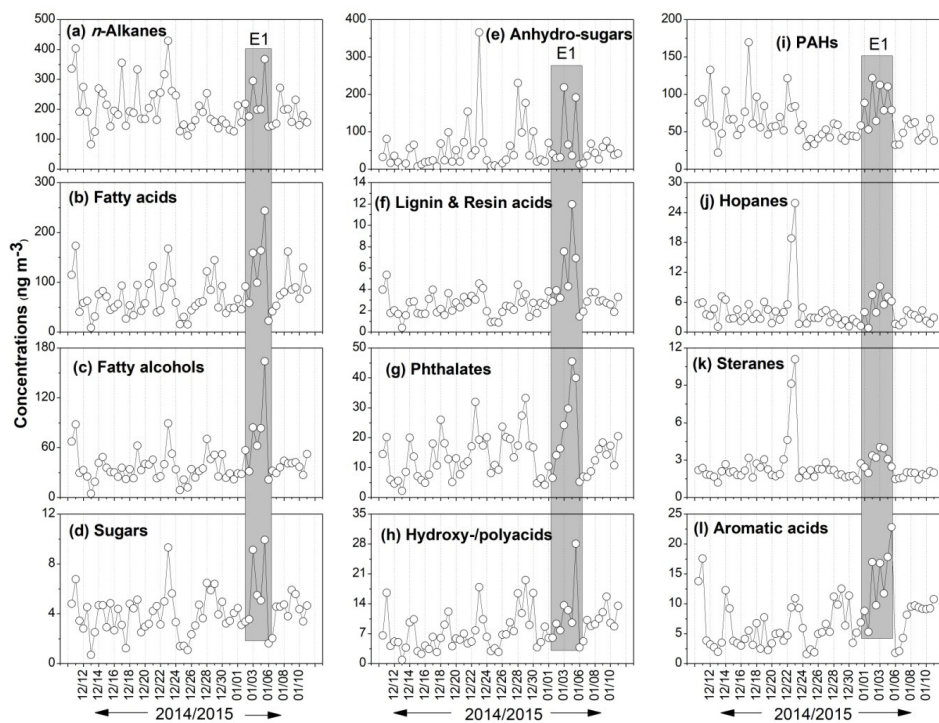
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1093   **Figure 3.** Temporal variations in the concentrations of organic compound classes detected in
1094   the Nanjing urban aerosols.

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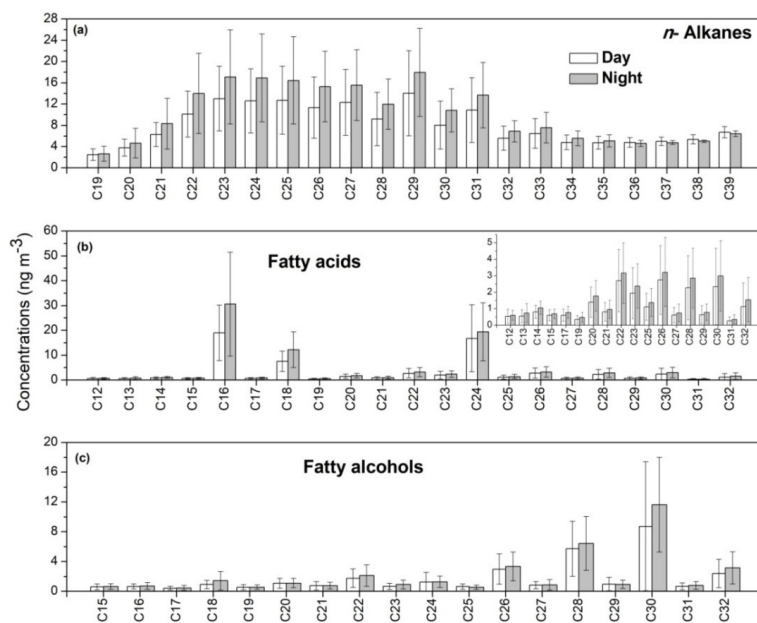
Figure 4. Molecular distributions of *n*-alkanes, fatty acids and fatty alcohols in $PM_{2.5}$
aerosols collected from Nanjing, China. Inner panel of b represent correspondence
carbon of fatty alcohols which concentrations are low.

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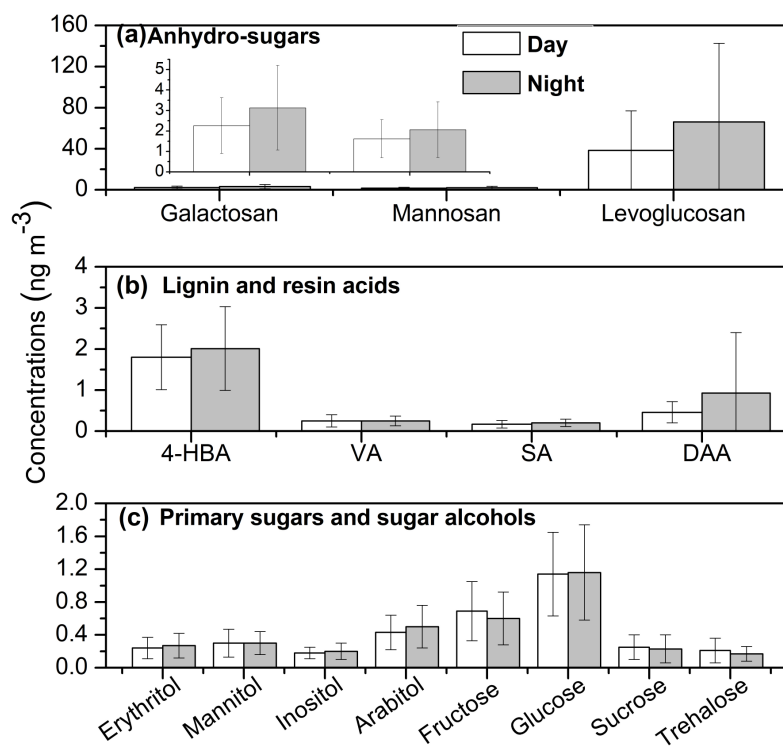


Figure 5. Molecular distributions of anhydro-sugars, lignin and resin acids and sugars/sugar alcohols in Nanjing aerosols. [4-HBA: 4-hydroxybenzoic acid , VA: vanillic acid, SA: syringic acid and DAA: dehydroabietic acid].

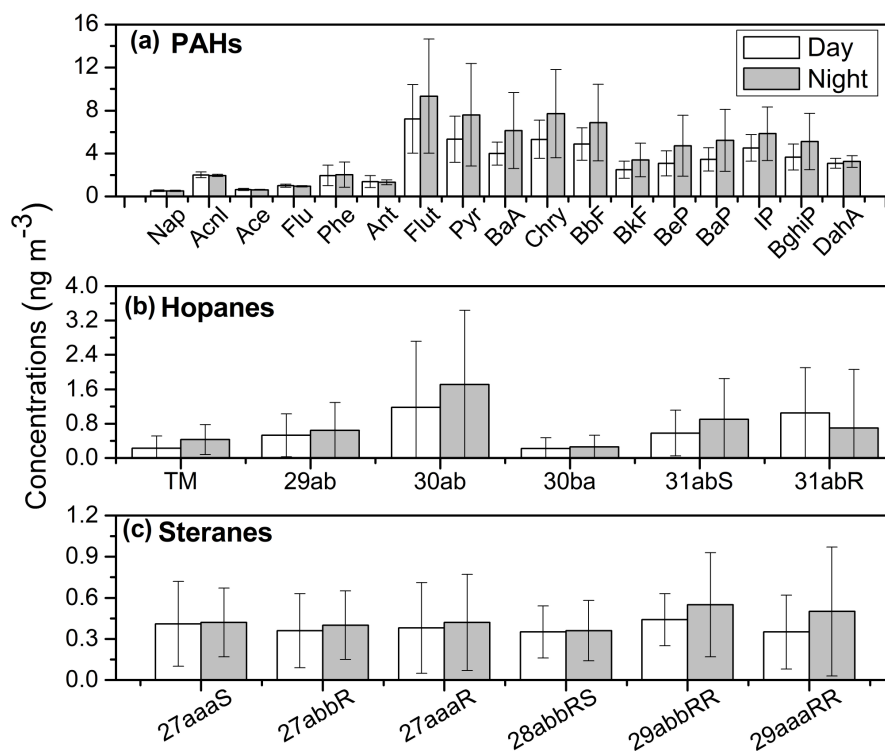
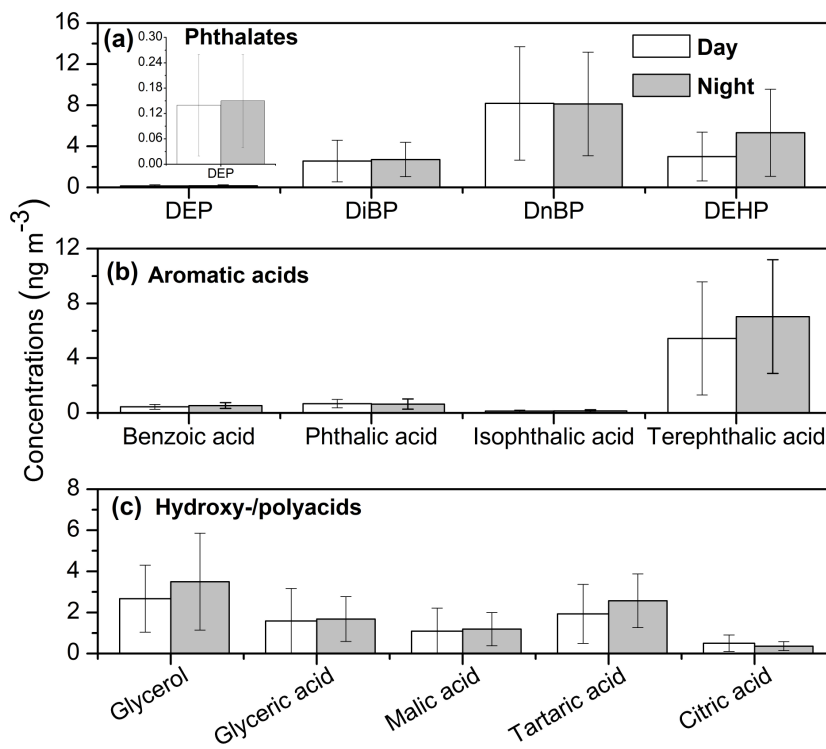



Figure 6. Molecular distributions of PAHs, hopanes and steranes in winter aerosols from Nanjing, China. [Abbreviation of PAHs: napthalene, Nap; acenaphthylene, Acnl; acenaphthene, Ace; fluorene, Flu; phenanthrene, Phe; anthracene, Ant; fluoranthene, Flut; pyrene, Pyr; benzo[a]anthracene, BaA; chrysene, Chry; benzo(b)fluoranthene, BbF; benzo(k)fluoranthene, BkF ; benzo(e)pyrene, BeP; benzo(a)pyrene, BaP; indeno(1,2,3-cd)pyrene, IP; benzo(ghi)perylene, BghiP; Dibenzo[a,h] anthracene, DahA].

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1117   **Figure 7.** Molecular distributions of phthalates, aromatic acids and hydroxy-/polyacids in
1118   Nanjing aerosols.
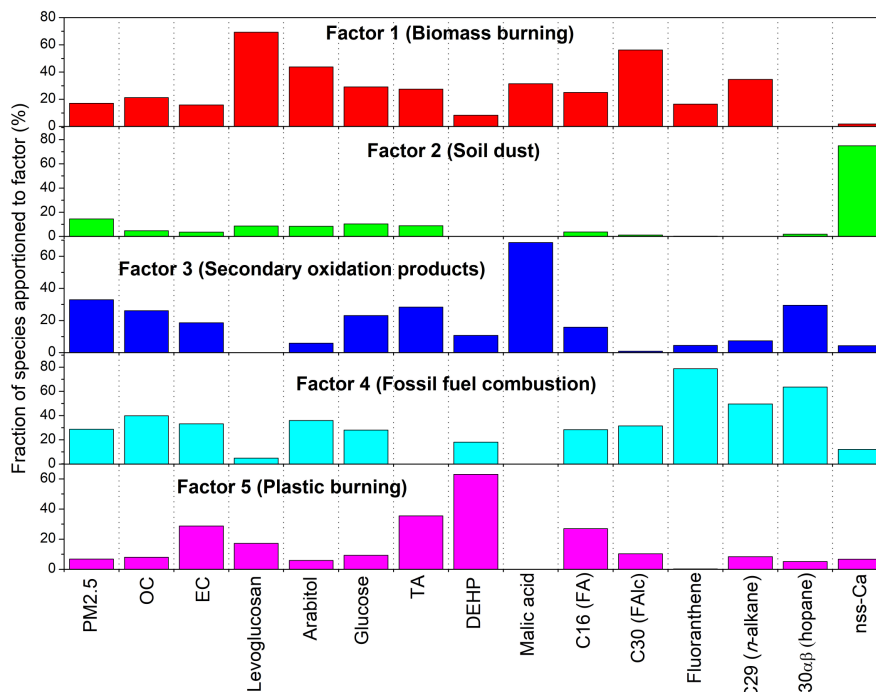
Figure 8. Composition profiles (% of total of each species) for the five factors resolved by PMF based on data from Nanjing winter aerosols from 11 December 2014 to 11 January 2015. [TA: terephthalic acid, DEHP: di-(2-ethylhexyl) phthalate, FA: fatty acid, FAlc: fatty alcohol].

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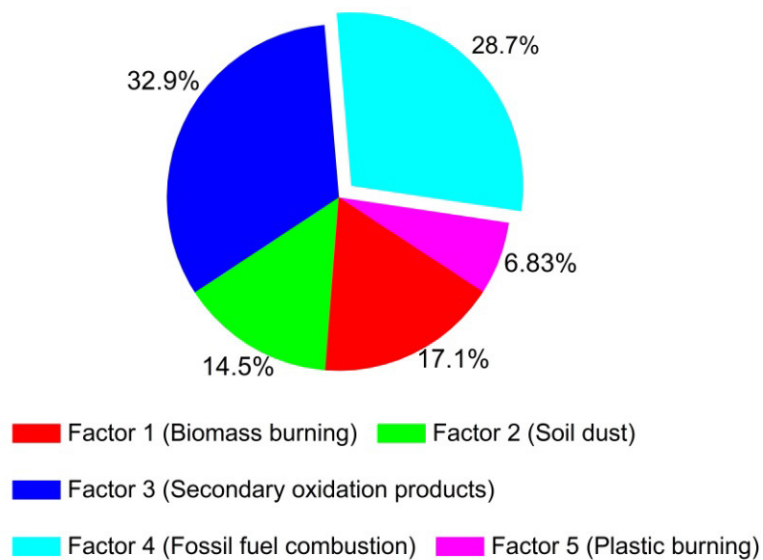
Figure 9. Pie diagrams showing the estimated source contributions of five factors
resolved by PMF to the PM$_{2.5}$ in Nanjing aerosols.

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